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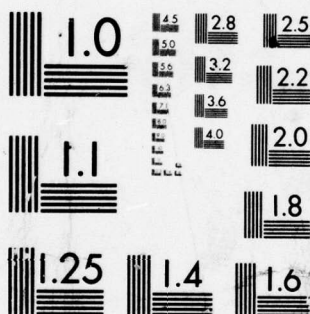
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PROGRESS REPORT

MASS-SPECTROMETRIC MEASUREMENTS OF ENHANCED METHANATION
ACTIVITY OVER COBALT AND NICKEL FOILS

BY

Robert L. Palmer and David A. Vroom

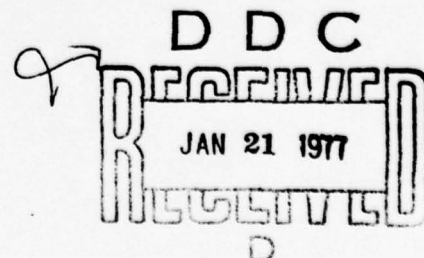
IRT Corporation
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December 20, 1976

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To be published in Journal of Catalysis



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Mass-Spectrometric Measurements of Enhanced Methanation Activity Over Cobalt and Nickel Foils.		5. TYPE OF REPORT & PERIOD COVERED Interim Report.
6. AUTHOR(s) Robert L. Palmer and David A. Vroom		7. PERFORMING ORG. REPORT NUMBER INTEL-8005-007
8. PERFORMING ORGANIZATION NAME AND ADDRESS IRT Corporation P. O. Box 80817 San Diego, CA 92138		9. CONTRACT OR GRANT NUMBER(s) N00014-72-C-0247
10. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Code 472 Chemistry Programs Office 800 N. Quincy, Arlington, VA 22217		11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 1220p.		13. REPORT DATE December 20, 1976
14. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		15. NUMBER OF PAGES 17
15. SECURITY CLASS. (of this report) Unclassified		16. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Catalyst, methanation, hydrogen, carbon monoxide, activation energy, molecular beams		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The kinetics of methane synthesis from H ₂ /CO mixtures has been studied over Ni, Co, and Fe foils. The gas composition of a flowing reaction cell was analyzed using a differentially pumped, modulated mass-spectrometer. Ni and Co foils that have been previously oxidized, and then reduced in H ₂ at 525-600°K show a surprisingly high and specific catalytic activity for methane formation. No unusual activity was observed over iron for any of the surface treatments tried here. Evidence is also presented to support a		

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Mass-Spectrometric Measurements of Enhanced Methanation Activity Over Cobalt and Nickel Foils

Robert L. Palmer and David A. Vroom

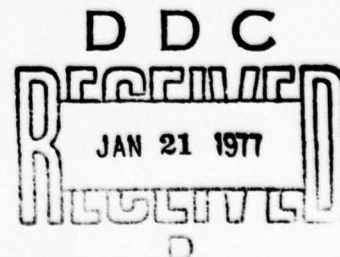
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ABSTRACT

The kinetics of methane synthesis from H_2/CO mixtures has been studied over Ni, Co, and Fe foils. The gas composition of a flowing reaction cell was analyzed using a differentially pumped, modulated mass-spectrometer. Ni and Co foils that have been previously oxidized, and then reduced in H_2 at 525-600°K show a surprisingly high and specific catalytic activity for methane formation. No unusual activity was observed over iron for any of the surface treatments tried here. Evidence is also presented to support a mechanism for this highly specific reaction involving a labile surface carbon atom intermediate.

INTRODUCTION

Renewed interest in the industrial scale synthesis of methane and other hydrocarbons has stimulated a number of recent studies of the catalytic conversion of CO/H_2 mixtures (1-6). The application of several new experimental methods to this problem promises to greatly expand our knowledge of methanation catalysis and, hopefully, lead to the development of catalyst materials with improved selectivity and poison resistance. We have relied primarily on



molecular beam techniques to investigate the mechanisms and kinetics of simple catalytic reactions (7-9) and have recently turned our attention to the reaction of CO with H₂ over the group VIII metals.

Using a differentially pumped line-of-sight modulated mass-spectrometer system, we have investigated the conditions for maximum catalytic methanation activity over the group VIII metals. This paper describes the surprisingly high activities observed on specially treated high purity (MRC Marz grade) cobalt and nickel foils whereas iron and other of the group VIII metals display much lower activities, in the range usually reported for supported catalysts.

EXPERIMENTAL METHODS

In order to more readily survey the activity of various catalytic materials and operating regimes, the usual molecular beam vacuum apparatus was slightly modified as shown in Fig. 1. In this arrangement, a catalytic reaction cell replaces the usual beam source and the mass-spectrometer detector is positioned directly in the line-of-sight path defined by the molecular beam apertures. Thus, we very readily achieve a differentially pumped line-of-sight modulated mass spectrometer system that can be used to sample the composition of the gas which flows through a small orifice (.010"-.020" dia) in the wall of the reactor cell. Indeed, accurate kinetic data can be obtained by this arrangement if the conditions within the cell are such that the reaction is kinetically limited and the gas composition is relatively uniform. These requirements are easily satisfied at low total conversions and for pressures within the cell in the 1.0 Torr range or below.

The data reported here were obtained using a reaction cell constructed as shown in exploded view in Fig. 1. The catalyst foil with dimensions $0.5 \times 4.5 \times .005$ in is formed into a closed spiral and inserted tightly into a $1\text{-}3/8$ in long inert metal (tantalum) heating tube as indicated in Fig. 1. Tantalum wafers are positioned against the open ends of the catalyst foil spiral and, finally, machined stainless steel caps are inserted over the ends of the tantalum tube. These end caps fit into water cooled stainless steel rods that are part of the normal beam source apparatus. The reaction cell is resistively heated by passing current through the cell via the end caps which remain relatively cool by virtue of the water cooled support rods.

In operation, various gases and gas mixtures can be circulated through the cell via one of the end caps, through a small hole in the center of the tantalum wafer and into the catalyst foil region. After circulating around the foil spiral, the gas flows out a small hole (0.010'' - 0.020'' dia) drilled through the outer tantalum tube and the outer wall of the catalyst foil. The other end cap leads to a capacitance type manometer (Validyne Model DP7) and normally no gas flows in this section of the line. The temperature of the cell is monitored by means of a thermocouple attached to the outside wall of the cell and, above 1000°K , with an optical pyrometer by looking into the cell via the line-of-sight path through the mass-spectrometer. The temperature uniformity of the cell appears to be adequate for the present experiments, although some degree of temperature variation undoubtedly exists within the cell. However, the thermocouple and pyrometer temperatures were within 20°K at 1000°K for various positions of the thermocouple and the temperature uniformity was undoubtedly enhanced by the high thermal conductivity of the hydrogen inside the cell during the methanation studies.

The surfaces of the catalyst foils were cleaned in situ by alternate oxygen and hydrogen exposures at elevated temperatures. Reduction at temperatures as high as 1400°K was used to remove all surface oxygen. Various temperature and exposure cycles were tried with reproducible results indicating that surface contamination, either from the gas phase or from the bulk, was not a problem. Research grade gases flowing through baked-out stainless steel lines contained less than ppm levels of impurities as determined directly by mass-spectrometric measurement. Thus, the system is quite clean compared with typical flowing catalytic reactor systems while possibly still being relatively contaminated when compared with surfaces prepared under UHV conditions. This is an advantage from one point of view since this system provides conditions intermediate between typical high pressure (one atmosphere and above) catalytic reactors and UHV single crystal studies.

RESULTS AND DISCUSSION

Using this experimental arrangement, methane production was observed over the high temperature reduced surfaces of Ni, Co and Fe in the expected temperature range of $525\text{--}600^{\circ}\text{K}$. The H_2/CO mixture ratio was typically kept at about 40:1 H_2 to CO to maintain a carbon free surface. High H_2 to CO ratios are also required to maintain approximately equal surface concentrations of these gases because of the higher heats of adsorption of CO on these surfaces. In the course of this work it was observed that a greatly enhanced methanation activity could be obtained over Ni and Co if these surfaces were reduced, after oxygen exposure, at methanation temperatures ($525\text{--}600^{\circ}\text{K}$)

rather than at high temperatures (above 800°K). No procedure could be found which resulted in any extraordinary activity in the case of Fe, however.

For the conditions reported here, oxygen pretreated Co is more than an order of magnitude more active than similarly prepared Ni foil. The activities in Figs. 2 and 3 are expressed as turnover numbers,

$$N = \frac{\text{product molecules}}{\text{metal site} \cdot \text{sec}}$$

which were calculated on the basis of 10^{15} metal sites/cm² and the geometrical area of the catalyst foil. However, exposure of the foil to oxygen increases the surface area somewhat and this factor coupled with other uncertainties in the calculation make the absolute values of the turnover number similarly uncertain. Thus, we have likely overestimated the turnover numbers in both Figs. 2 and 3 by about a factor of 2. However, these turnover numbers are for a total pressure of 2 Torr, whereas methanation rate data are usually reported for pressures of one atmosphere.

In addition to CH₄, which was detected as CH₃⁺, H₂O was also observed mass-spectrometrically during methanation in quantities comparable with methane. Small amounts of CO₂ could also be detected as a reaction product but its rate was very slight in excess hydrogen where high methanation rates were observed. Other higher hydrocarbon products such as ethylene, ethane, etc., as well as alcohols were looked for but not observed. On activated Ni and Co foils under reaction conditions where high methanation rates were observed, hydrocarbons other than methane, if any, must constitute substantially less than 1% of the reaction product.

Temperature Dependence

Data for the temperature dependence of the catalytic activities of Ni and Co foils reduced at 525-600°K after oxygen exposure at 800°K are given in Fig. 2. For these measurements the H₂/CO ratio was maintained at 40:1 at

a total pressure inside the cell of 2 Torr. With a 0.020 in orifice in the cell the flow rate is such that the gas mixture spends, on the average, 3×10^{-2} sec within the catalyst cell volume (2.3 cm^3).

The temperature dependence data were reversible for temperatures below 600°K . At higher temperatures the data points represent initial rates which slowly decayed to much lower steady-state values. This decay was irreversible with temperature, but the initial activities of both Ni and Co foils could be restored by exposure to oxygen followed by reduction at $525\text{--}600^\circ\text{K}$. At temperatures above 600°K graphite formation becomes rapid on these surfaces and it is believed that the surface becomes deactivated at these temperatures as the result of the formation of a stable graphite overlayer. The slope of the temperature dependence data of Fig. 2 indicates an activation energy of 17 ± 1 kcal/mole for the rate limiting step on both foils.

H_2/CO Dependence

Figure 3 presents methanation rate data at 550°K over Co foil, prepared as in Fig. 2, as a function of the H_2/CO ratio. The rate is seen to be approximately first order in CO concentration up to 0.6% CO, then approximately zero order to 4% CO. The data below 4% were stable and reversible. Above 4% CO concentration there was a rapid irreversible decrease in the rate. The data points in Fig. 3 from 4% to 20% CO are steady-state rather than initial values and represent apparently steady-state values obtained after operating for about one hour at each point. When all of the CO was removed from the gas flow after the last data point at 20% CO was taken, a slow but detectable rate of CH_4 formation still persisted with only H_2 gas flowing through the cell. Replacement of the H_2/CO mixture with O_2 gas in the cell at 550°K produced strong CO and CO_2 signals at the mass-spectrometer that persisted for a long period. These results suggest that the catalyst

foil had absorbed a large amount of carbon into the bulk during operation at CO concentrations greater than 4%. The full catalytic activity of the Co foil could be restored by repeated oxidation-reduction (O_2 - H_2) cycles at higher temperatures to remove all carbon with the final reduction cycle carried out at 525-600°K.

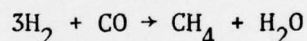
Surface Conditions

Our inability, in this experiment, to directly investigate the catalyst surface composition and structure in situ, e.g., via LEED, AES and photoelectron spectroscopy, leaves us with only indirect inferences regarding the catalyst surface conditions during this experiment. The data of Figs. 2 and 3 may or may not be representative of methanation activities over clean polycrystalline Co and Ni. Certainly oxygen exposure at elevated temperatures should have removed most of the near-surface carbon, the most probable impurity in this work. Also, oxidation-reduction cycles increase the surface areas somewhat through roughening, as evidenced by the matte finish the shiny foils acquire during this procedure. Thus, a somewhat higher activity after oxidation-reduction cycles is not surprising. However, the Fe foil was not particularly affected by this treatment and its activity for methanation was down by more than an order of magnitude from Ni and two orders less than Co. Thus, the activity of iron is in the range reported by Vannice at one atmosphere ($N \leq 0.1$) (1), whereas the activities of Ni and especially Co appear to be anomalously high. Reduction by exposure to hydrogen at higher temperatures, above 800°K, drastically lowers the activities of Co and Ni down to levels comparable to Fe. This observation suggests that oxygen may be playing a role other than just to simply remove surface contaminants. Auger analysis of the highly active foil surfaces was carried out in a separate ultra-high-vacuum facility and revealed about 2% oxygen, even after removal of the first few surface layers by ion

sputtering. Although low levels of oxygen are not surprising, even without deliberate oxygen exposure, its presence is further suggestive of its possible role in enhancing the catalytic activities of Ni and Co. Carbon was the only other detectable surface impurity by Auger analysis.

Adsorption Kinetics

From the data of Fig. 3 it is obvious that at H_2/CO ratios approaching stoichiometric, the catalytic activity of Co (and Ni) falls off drastically due both to poisoning from excess surface carbon at CO levels above 4% as well as kinetically unfavorable concentrations of H_2 and CO on the surface. Using typical values for heats of adsorption on Ni of 18 kcal/mole for hydrogen and 28 kcal/mole for CO (10), at 550°K the ratio of surface concentrations of H_2 to CO, at equal adsorption rates, is about $1:10^4$. At our typical H_2/CO ratio of 40:1, the surface concentrations would then be about 1:250 H_2/CO . For the overall reaction

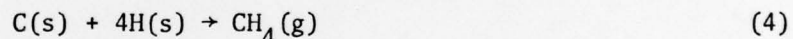
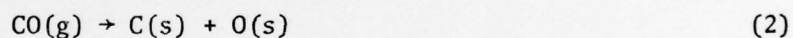


we need a surface concentration of H_2 three fold greater than CO. This suggests that, from a kinetics point of view, the proper H_2/CO ratio in the gas phase for maximum methanation rate should be roughly $3 \times 10^4:1$ H_2 to CO. The observation here that the kinetics are optimized at substantially lower H_2/CO ratios implies that, once on the surface, CO is proportionately less reactive than H_2 (which is presumably chemisorbed as highly reactive atoms). In the foregoing arguments we have neglected the probable effect of different adsorption (sticking) probabilities for H_2 and CO. Usually, the sticking probability of H_2 is found to be greater than 0.1 on these surfaces (11-13). However, for surfaces partially covered with CO and other adsorbates and impurities such as carbon, the adsorption rate of H_2 very likely decreases to significantly below that of CO (14,15). This factor acts to decrease the equilibrium surface concentration of H_2 relative to CO even further. Thus, under kinetically ideal

conditions, it appears probable that the reactivity of surface CO is rate limiting, as has often been suggested (16). The most sensitive parameters in this argument are the relative heats of adsorption of H_2 and CO although the chemisorption of H_2 may also be quite sensitive to CO coverage as well (14). Since methanation is usually carried out with nearly stoichiometric H_2 /CO gas mixtures, the surface in this regime is so overwhelmingly dominated by adsorbed CO that H_2 adsorption is limiting in this case as indicated by the build-up of excess surface carbon. Again, these arguments are tentative in the absence of accurate heat of adsorption data for the precise surfaces and adsorbate coverages encountered under methanation conditions.

Reaction Mechanism

The simplest mechanism to consider for the surface process leading to methane formation is the following:



although other mechanisms involving various intermediates such as HCO have been suggested (4,16). Steps (3) and (4) are assumed to occur in a step-wise manner in which H atoms are added sequentially since this is kinetically much more likely. Step (2) is perhaps the most suspect but its rate can be estimated by means of the disproportionation reaction



which can easily be measured with our apparatus. We observe that the initial rate of (5) in the absence of hydrogen is comparable with the peak methanation rate at the same temperature, so it appears that step (2) proceeds at

approximately the correct rate to be considered as the primary reaction path for methanation. Thus, we presently favor the view that methanation proceeds via a labile carbon intermediate, whereas at temperatures above 600°K, graphite formation deactivates this carbon and poisons the catalyst surface. Further direct surface studies will, of course, be necessary in order to confirm this suggestion.

RELATED STUDIES

Numerous studies relative to H_2 and CO chemisorption on the group VIII and other metal surfaces have appeared in the literature since the work of Sabatier at the turn of the century. Because of the widely diverse results included in this work, a similarly diverse range of points of view can be supported by judicious choice of reference literature. However, it is tempting to cite some fairly recent surface studies involving H_2 and CO that bear on the present work.

One of the few published studies of methanation at high H_2/CO ratios is the recent work of Fontaine (4). He studied Ni supported on SiO_2 for $H_2/CO = 50/1$ in the temperature range 485-598°K. Although his turnover rate was apparently quite low he observed an activation energy of $18 \pm .5$ kcal/mole for the methanation reaction, in close agreement with the results reported here.

Regarding activation of Ni and Co foils it is interesting to note that Selwood has observed very rapid ortho-para conversion of hydrogen over Ni oxide supported on alumina when reduced in hydrogen in the range 673-763°K (17). But when the same catalyst is reduced at 873°K the catalytic activity is reduced by more than two orders. This is the temperature range where a

similar loss of activity was observed in the present study and suggests that sites with high activity for non-dissociative ortho-para conversion are also very active for methanation catalysis.

There is apparently some controversy about the rate of CO dissociation on Ni and Co surfaces. On single crystal surfaces at room temperature the rate is evidently too slow to be detected for exposures typically used in adsorption studies. However, Madden and Ertl have studied the adsorption of CO on Ni(110) and found that when this surface is heated in CO the CO dissociates into individually bound carbon and oxygen atoms (18). The oxygen atoms are then rapidly removed by reaction with CO to form CO_2 . Tottrup, in a separate study of the Boudouard (disproportionation) reaction over alumina supported Ni found that both H_2 and H_2O have a small retarding effect on the reaction (19). These results are consistent with the view that methanation proceeds via a labile surface carbon intermediate and that surface hydrogen does not enhance the scission of CO molecules on the surface through the action of a hydrogen containing intermediate such as HCO.

SUMMARY

The experimental method used in this work allows rapid and accurate measurements of reaction products over a wide range of experimental conditions, and in a pressure regime intermediate between high vacuum "clean" surface studies and typical flowing reactor systems. By operating under kinetically ideal conditions, we have been able to study the catalytic methanation activity of several group VIII metal foils which were prepared by various procedures. The results indicate that very substantial changes in catalytic activity can be achieved over surfaces prepared under slightly different conditions. The application of the highly active catalyst surfaces produced in this work to

practical large-scale methanation is still questionable at this point. However, a more thorough understanding of the important parameters in this reaction may suggest ways of improving the process.

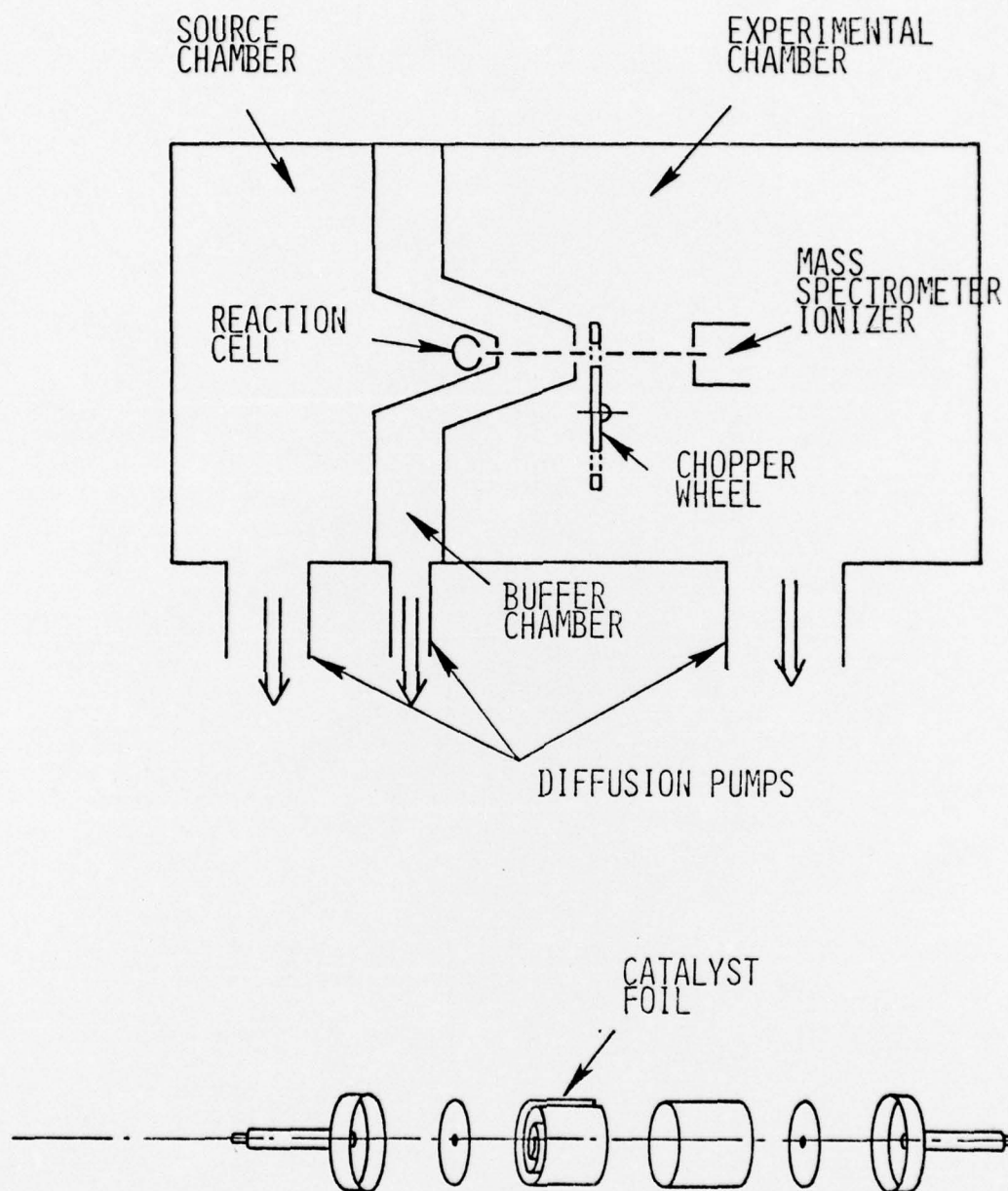
Further studies are suggested by the present results, including detailed surface studies to determine features associated with the high catalytic activities seen here. Also, related studies should be carried out at higher pressures to determine catalytic behavior in the usual methanation regime.

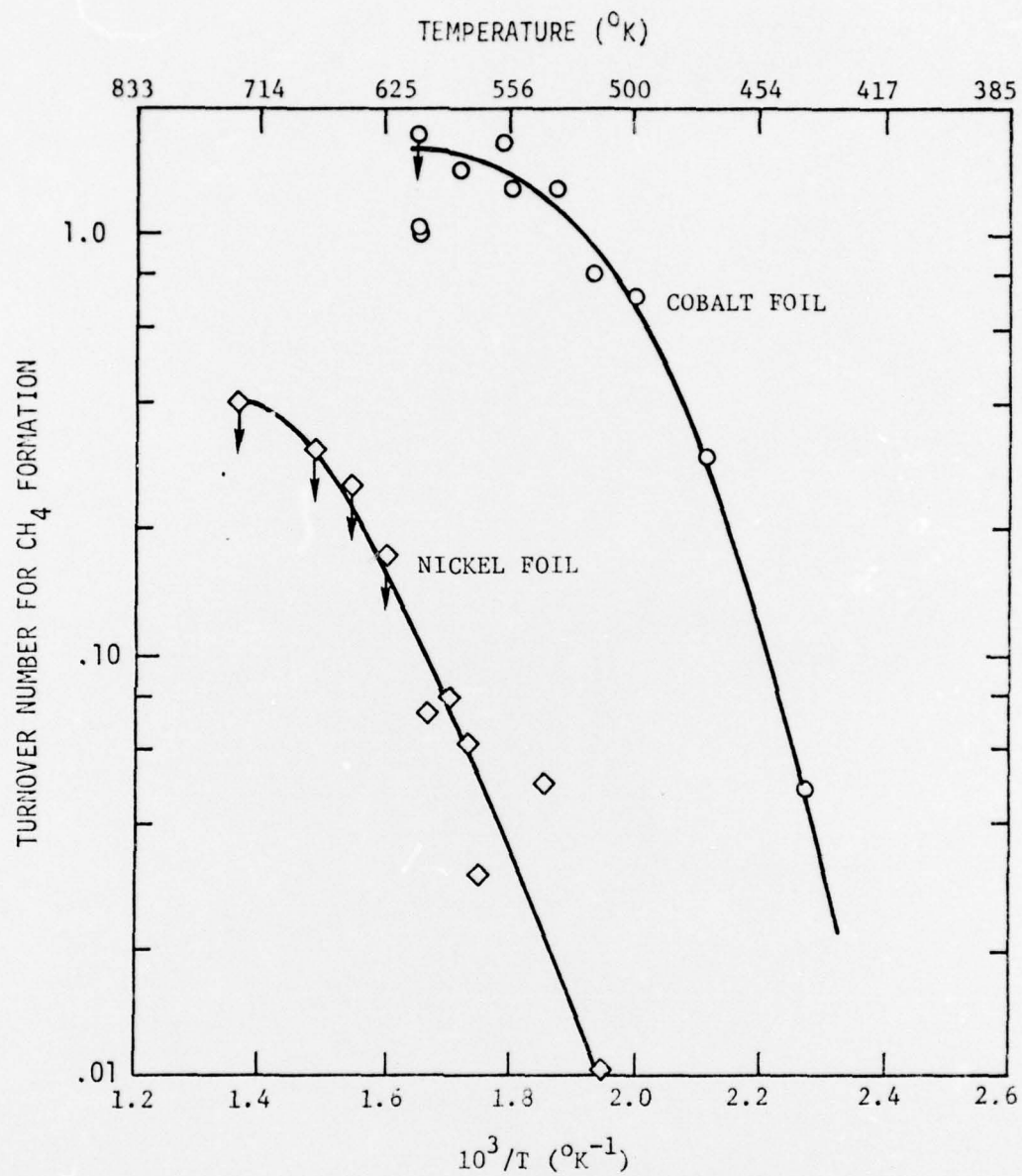
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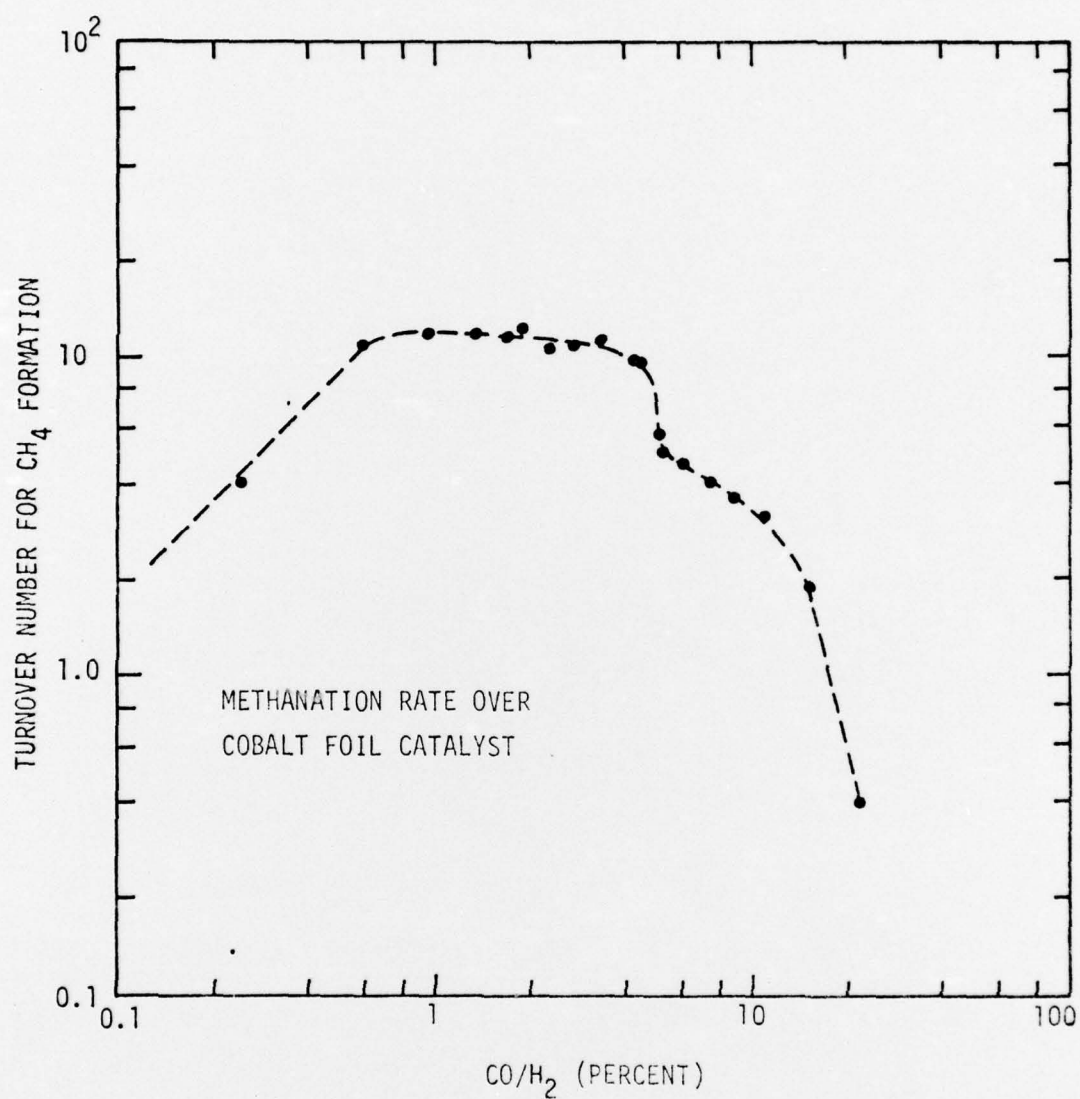
FIGURES

1. Schematic of differentially pumped modulated mass-spectrometer and exploded view of reaction cell construction.
2. Arrhenius plots of mass-spectrometer (CH_3^+) data over activated Ni and Co foils at H_2/CO ratio of 40:1 and total pressure of 2 Torr. Turnover numbers based on geometrical foil area.
3. Methanation rate versus CO/H_2 ratio over activated Co foil at 550°K and total pressure of 3 Torr. Turnover numbers based on geometrical foil area.





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